



Carbon blacks for lead-acid batteries in micro-hybrid applications – Studied by transmission electron microscopy and Raman spectroscopy

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H I G H L I G H T S

- Lead-acid starter batteries with different carbon blacks in the negative active material were cycled in typical PSoC tests.
- Batteries with highly ordered carbon blacks in the NAM showed superior cycle life in the 17.5% DOD test.
- Electrical data have been complemented by SEM, TEM and Raman investigations.

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Micro-hybrid vehicles with stop–start function and regenerative braking lead to higher requirements on flooded lead-acid batteries. A promising approach to improve the cycleability of flooded lead-acid batteries is the use of carbon additives in the negative active mass. In this study different carbons (carbon blacks and a lamp black) were studied by transmission electron microscopy and Raman spectroscopy. Furthermore, batteries containing carbon blacks and lamp black in the negative active material were cycled with 17.5% depth of discharge. Morphology, surface functionalisation, and the degree of order were correlated with the cycle life. In cycling tests, batteries with highly ordered carbon blacks increase the lifetime of the corresponding battery by up to a factor of two.

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1. Introduction

Lead-acid starter batteries employed in micro-hybrid vehicles undergo strong cyclic loads, because they are operated in a partial state of charge (PSoC). High charging currents and exhaustive

discharges lead to an inhomogeneous density profile of sulphuric acid (acid stratification) used in flooded lead-acid batteries. An early loss of capacity can be observed during a PSoC-mode due to irreversible electrode processes, like sulphation, i.e. the irreversible formation of large lead sulphate crystals on the negative electrode. This results in an early capacity loss and therefore leads to battery breakdown. Numerous publications report about less sulphation on the negative electrode when carbon is incorporated into the negative active material (NAM) [1–4]. It has been suggested that carbon impedes the growth of lead sulphate crystals [5]. Carbons exhibit a high corrosion stability, are conductive, light-weight materials, easy to handle and can be obtained in different modifications [6]. Many studies refer to valve-regulated lead-acid (VRLA)

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batteries, using different carbons in the NAM [2–5]. In previous studies on the influence of different carbon additives on battery performance, the focus was put mainly on macroscopic properties, as e.g. BET surface or particle size [1,3]. Mechanistic discussions on how the carbons act are still on-going and based on experimental techniques like scanning electron microscopy (SEM), cyclic voltammetry, and cycling at high-rate partial-state-of-charge (HRPSoc) of AGM test cells (AGM: Absorbent Glass Mat, the electrolyte of this battery-technology is held in a glass mat) [1,7].

In this work, the focus is put on enhanced flooded lead-acid batteries (EFB), i.e. flooded batteries with thicker grids showing improved corrosion resistance, and with a fleece support for keeping the active material coherent and using carbon blacks (CBs) in the NAM. BET surface, pore volume, average particle size, and dry powder resistivity of the investigated CBs are provided in Table 1.

The internal structure of carbon-black aggregates is not well understood [8]. In previous studies graphite-like, crystalline-like domains, in which basal planes are parallel, but distorted, have been detected in CB-particles [8]. Biscoe and Warren describe the CB as an intermediate form of matter, which is different from the amorphous and the crystalline states [9]. They suggest “turbostratic” (unordered layers) as a suitable name for these mesomorphic carbons. Based on this definition, CB structures would be described as consisting of turbostratic groups. Each group consists of some graphene-like layers that are stacked together roughly parallel and are almost equidistant, but have a completely random orientation [9].

In the first part of this paper, the characterisation of CBs regarding morphology as well as surface modification is described by transmission electron microscopy, X-ray diffraction, and Raman spectroscopy. The determination of structure–property relationships on the microscopic scale is certainly important because an understanding of the carbon effect could lead to a better understanding of the underlying mechanisms. The second part of this paper is devoted to the cycling of EFBs with the corresponding CBs in the NAM. Fundamental aim of this research is to establish a correlation between the material characteristics of the different CBs and the cycle lifetime of the batteries with the respective CBs in the NAM. To eliminate the influence of the total surface area of CB in the NAM on cycling performance and thus to focus on structural properties, the carbon content in each battery was normalized to the BET surface. The estimated carbon surface area was this way kept constant at $\sim 0.5\text{--}0.6\text{ m}^2\text{ g}^{-1}$, as shown in Table 2.

2. Experimental

2.1. Materials synthesis and characterization

2.1.1. Preparation of the carbon blacks and the lamp black

The CBs were synthesized in the most modern furnace black process [10]. The LB was produced in the standard process [10].

2.1.2. Surface modification of carbon black with sulphonilic acid groups

The treatment of carbon with sulphonilic acid groups was done by the diazonium salt reaction method, as described in a US patent

Table 1
BET surfaces, average particle sizes, pore volume and dry powder resistivity of the examined CBs and LB.

	CB No. 1	CB No. 2	CB No. 3	CB No. 4	LB
BET-surface [$\text{m}^2\text{ g}^{-1}$]	243	58	54	153	29
Average particle size [μm]	3.8	4.2	6.2	0.05	2.1
Pore volume [$\text{cm}^3\text{ g}^{-1}$]	0.51	0.20	0.19	0.71	0.05
Dry powder resistivity at 470 kg cm^{-2} [$\text{m}\Omega\text{ cm}$]	77	88	79	4224	51

Table 2

Amounts of CBs and LB used in the active masses.

	CB No. 1	CB No. 2	CB No. 3	CB No. 4	LB
Mass in relation to the NAM [%]	0.2	1.0	1.1	0.3	2.0
Expected surface area of carbon in the NAM [$\text{m}^2\text{ g}^{-1}$]	0.5	0.6	0.6	0.5	0.6

by Belmont et al. [11]. Further purification of the treated carbon was performed to remove residuals of the diazonium salt treatment.

2.1.3. Transmission electron microscopy

Transmission electron microscopy (TEM) was employed to characterise the respective CBs in size, morphology, and aggregate structure. Therefore, a small amount of the samples was highly dispersed in 2-propanol. A drop of the dispersion was dripped on a perforated carbonaceous TEM-grid. Then, the solvent was evaporated carefully under red light. The TEM investigations were carried out at a JEOL JEM-2100F field-emission transmission electron microscope (FE-TEM). The excitation voltage was at 200 kV. Bright-field images were recorded for determining the particle size and morphology. The degree of ordering of turbostratic carbon was analysed by high-resolution TEM and selected area electron diffraction (SAED).

2.1.4. Raman spectroscopy

Raman spectra of the different carbon species were measured with a Raman microscope (Olympus BX 41 linked to a DILOR XY-800 from HORIBA Jobin-Yvon) using the second harmonic of a Nd:YAG-Laser (532 nm) as light source and a CCD-camera (Synapse from HORIBA Jobin-Yvon). Finely ground carbon powder was dispersed on a turntable under the microscope to provide a large sample area for suitable averaging as well as heat dissipation. To decrease further the local radiation intensity, the measurements were done out of focus at a sample distance of 125 μm using an objective with 50-fold magnification. The resulting laser spot was about 50 μm in diameter. The power of the laser beam was adjusted in the range of 5–20 mW in order to avoid sample damage as well as fluorescence.

2.1.5. Determination of impurities

The amount of selected metal impurities in the CBs and the LB (iron, cobalt, copper, chrome, nickel, and manganese) was determined by the ash extraction method. 5 g of carbon was ashed in a muffle furnace at 650 °C for 12 h. The ash was digested initially with nitric acid, then with hydrofluoric acid. Then, the digestate was dried and further dissolved in nitric acid. The samples were analysed by peak-profiling inductively coupled plasma optical emission spectroscopy (standards with <0.5 ppm for all elements of interest).

2.2. Electrical testing

2.2.1. Cycles with 17.5% DoD

Batteries with 59 Ah nominal capacity and 640 A EN (cold crank current) were prepared in standardised design (LN 2-battery-container, according to EN-50342 [12]). The sample batteries were characterised after a pre-measurement with a capacity test and cold start test according to EN 50342-1 [12] with 17.5% depth of discharge. The tests were run according to the test procedure described in ref. [13], but without mechanical movement. Before and after cycling, the acid density was measured in relation to the height of the plate at two different points: 0% (0% conforms to the top of a plate) and 100% (100% conforms to the bottom of the plate). The measurements were carried out with a measurement device DMA 35N from Anton Paar.

2.2.2. Water consumption test

A water consumption test was carried out in order to quantify the electrolyte losses. In doing so, the batteries were overcharged with 14.4 V at 60 °C in four units. One unit of this test takes 21 days. The weight loss caused by the arising gassing was recorded.

3. Results and discussion

3.1. Carbon black characterization

Different aggregate structures of the CBs and the LB are shown in the TEM bright-field images in Fig. 1. The aggregates show sizes in the sub- μm scale. These images visualise the formation process of primary particles. All primary particles are nearly spherical-shaped and they are clustered in larger aggregates. The aggregate size of the CB particles No. 1, No. 2, and No. 3 ranges from 25 to 100 nm. The particle size of the functionalized CB No. 4 shows a smaller range from 25 to 50 nm compared to the other CBs. The largest size range is covered by the LB particles with 50 to 200 nm. Besides the difference in size, it is possible to assign the examined CBs to different aggregate shape categories [14]. CB No. 1, CB No. 2, and CB No. 3 belong to the class of ellipsoidal structures. CB No. 4 can be classified as a spherical structure and the LB reference shows branched aggregates. It is noteworthy that CB No. 4 has a cloud-like aggregate structure. The CB particles No. 1, No. 2, and No. 3 show a similar arrangement. Scattered areas are visible where the particles have many contact sites (black areas). Within those aggregates, many free spaces are visible. The CB No. 4 shows a completely different arrangement of its particles. They are densely packed, contact sites show off continuously and they have less free space. All particles show a porous structure and exhibit lamellar layer structures with a similar distance between the layers of 0.4 nm (Fig. 1) – except for CB No. 3. A layer distance of approximately 0.36 nm was determined for CB No. 3 (Fig. 1). The SAED pictures depicted in Fig. 1 show the development of diffuse Debye–Scherrer rings indicating a partial ordering of the turbostratic lamellae (sets of parallel panels, representing parallel layer groups, corresponding to graphitic layers) around the CB particles. The graphitic layers in all CBs tend to be continuous. Already in 1968, Hess and Ban [15,16] as well as Harling and Heckman [17] observed these continuous graphitic layers on phase contrast images of untreated CBs. All samples show negligible differences – except for CB No. 3. The Debye–Scherrer rings for CB No. 3 are less diffuse which indicates a higher degree of order than in the case of the other CBs.

From the SAED pattern shown in Fig. 1, radial intensity distributions were determined as depicted in Fig. 2. Every Debye–Scherrer ring shows up as a local maximum of the reciprocal distance from the primary electron beam. Maxima can be recognized and can be correlated to crystalline reflections 0002, 0004, and 0006 of graphite [9]. The main maximum of all CBs – except CB No. 3 – is located at 0.4 nm. For CB no. 3 a main maximum at a smaller distance of 0.36 nm can be found and the Debye–Scherrer rings appear less diffuse. Both details indicate a higher degree of order, as already observed in the HRTEM micrograph (Fig. 1) of the turbostratic CB.

A more quantitative discussion of carbon black structures can be derived from Raman spectra of the different carbons. Raman spectroscopy allows us to estimate the relative concentration of amorphous carbon on the surface of carbon blacks aggregates [8]. In Fig. 3, Raman spectra are shown that are in the range for typical Raman-active bands of carbonaceous materials (here CB No. 3 and LB). As typical for turbostratic carbons, the main vibrational features are bands at $\sim 1350\text{ cm}^{-1}$ (D-band, symmetry: A_{1g} , disordered) and $\sim 1580\text{ cm}^{-1}$ (G-band, symmetry: E_{2g} , graphitic). The

shape of these peaks depends on the crystallite sizes [8,18]. In between, a weak and broad band appears which is correlated to sp^3 -like structures (A-band, 1500 cm^{-1} , amorphous structures) [19,20]. Its intensity relative to that of the D- and G-band is an estimate of the relative concentration of amorphous carbon on the surface of carbon black aggregates [8]. The size of amorphous domains decreases in the order $\text{LB} > \text{CB No. 2} > \text{CB No. 1} > \text{CB No. 4} > \text{CB No. 3}$.

As the G-band is the main vibrational mode of ideally ordered graphite and the D-band can be assigned to nano-sized crystallites in disordered structures, the D/G-intensity-ratio is a well-established criterion for the mean size of graphitic domains and thus for the degree of order [19–21]. The peak assignment is done according to Jawahari et al., whereas the fitting procedure for the measured data sets could be improved by using Voigt-profiles instead of single Gaussians or Lorentzians [19]. The medium lateral crystallite size L_a of graphitic domains is determined from the D/G-intensity-ratio according to Tuinstra and Koenig [21]:

$$L_a/\text{nm} = 4.35 \cdot I_g/I_d \quad (1)$$

(I_g : G-mode intensity, I_d : D-mode intensity).

In general, all spectra show broad D- and G-bands indicating rather small crystallite sizes and a relative high degree of disorder. Only CB No. 3 shows relatively sharp bands and a very weak intensity in the A-band region, which is a hint for higher structural order [20]. Quantitative spectral parameters as well as the L_a -values are given in Table 3. While all other carbons exhibit low L_a values in the range of 1–1.6 nm, CB No. 3 shows a value of 3.2 nm which is two to three times higher. Thus, it can be concluded that CB No. 3 shows a significantly higher degree of structural order arising from larger graphitic domains. This feature is also referred to as high graphitization. These results are consistent with the conclusions derived from the SAED measurements.

3.2. Electrical cycling tests

To exclude manufacturing defects and inequalities among the batteries, significant parameters were checked before the batteries were employed in the test facility. The parameters analysed are the open-circuit voltage (OCV), the internal resistance (R_i) (measured by internal resistance analyser Hioki 3554), as well as the weight of the batteries. The data are compiled in Table 4.

In Fig. 4 the development of the end-of-discharge voltage from the 17.5% depth of discharge cycled batteries with the respective CBs and the LB are plotted against the number of cycles.

Apparently, the battery that contains the most ordered CB (CB No. 3) in the NAM has the highest cycling lifetime in comparison to the other batteries and reaches close to 1000 cycles vs. 500 cycles for LB and CB No. 1 and 370 resp. 230 cycles for CB No. 4 and No. 2. As a comparison: A conventional flooded lead acid battery reaches in the test (with mechanical movement), described in ref. [13] about 200 cycles. In Fig. 5 the cycle number is plotted against the L_a values from the Raman measurements. It can be seen that a higher degree of order favours the cycle life. The data do not even account for a linear relationship; also a non-linear behaviour with higher carbon loads is possible. An interesting effect is the fall-off of the end-of-discharge voltage curve of the battery with the CB No. 3 after 500 cycles and the subsequent slope of the curve, this anomaly is under present investigation.

Due to processing, the examined CBs show small amounts of impurities (Table 5). Iron is detected in all specimens as the main impurity. In CB No. 4 iron, nickel, and copper can be found in higher concentration (Table 5). Other impurities are negligible because they were found to be lower than the detection limit of the

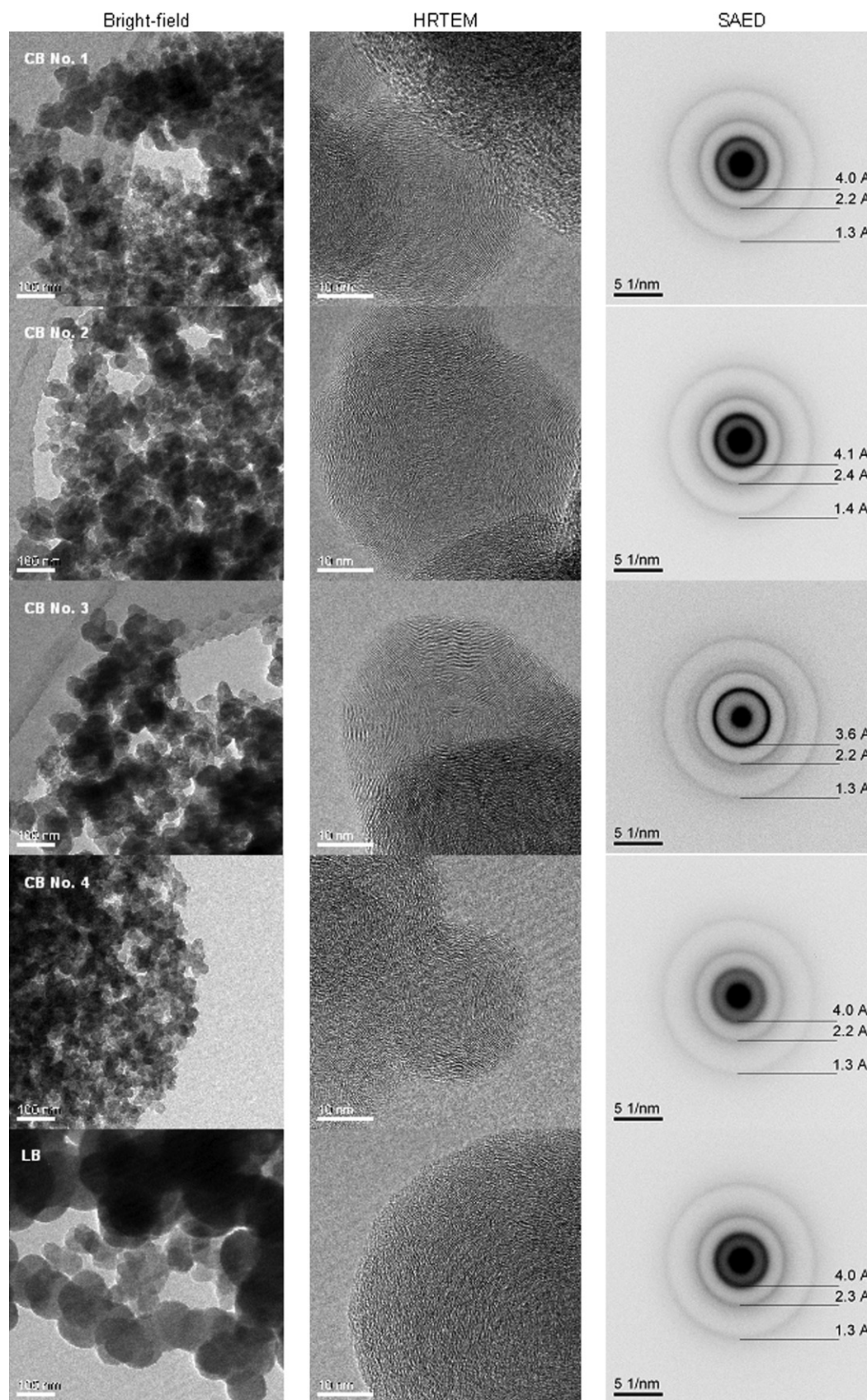


Fig. 1. CB No. 1 to 4 and LB (from top to bottom): TEM bright-field images, HRTEM and SAED pattern.

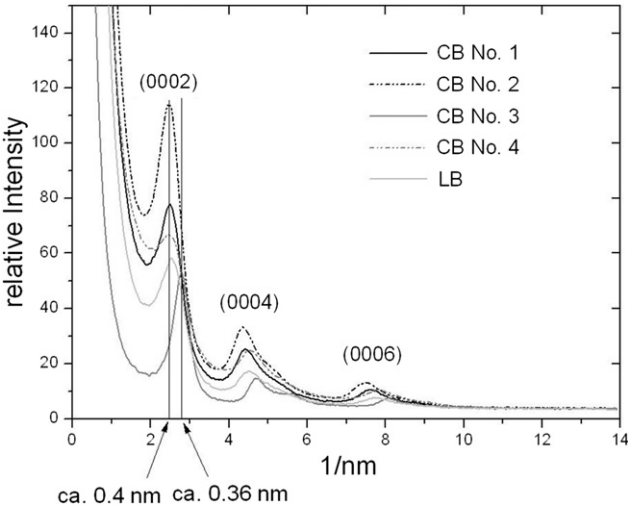


Fig. 2. Radial intensity distribution of the electron diffraction patterns of the CBs and the LB.

respective element. Carbons that contain impurities lower the overpotential of hydrogen evolution, leading to increased water loss, and eventually reduce the efficiency of charge [1,22].

Fig. 6 shows the water losses of the batteries with the different CBs and the LB during the overcharge test. It can be seen that the batteries with the CB No. 1, 4 and the LB show similar water consumption levels (Fig. 6). The batteries with the CB No. 2 and 3 show also similar water consumption levels, but they are clearly higher than the water losses of the batteries with CB No.1, 4 and the LB (Fig. 6). Obviously the high impurity levels in CB No. 4 do not lead to higher water loss. In combination with the water

Table 3
Raman-Peaks and calculated L_a values of CBs and LB.

	CB No. 1	CB No. 2	CB No. 3	CB No. 4	LB
Wavenumber [cm^{-1}]					
D-band	1352 ± 1	1357 ± 1	1358 ± 0.4	1360 ± 3	1358 ± 1
A-band	1539 ± 17	1500 ± 2	1499 ± 4.2	1519 ± 5	1559 ± 12
G-band	1609 ± 2	1599 ± 1	1597 ± 0.3	1604 ± 2	1605 ± 1
L_a [nm]	1.5 ± 0.3	1.3 ± 0.1	3.2 ± 0.2	1.6 ± 0.3	1.0 ± 0.4

Table 4
OCV [V], R_i [$\text{m}\Omega$] and weight [kg] of the tested sample batteries.

	Battery (CB No.1)	Battery (CB No. 2)	Battery (CB No. 3)	Battery (CB No. 4)	Battery (LB)
OCV [V]	12.71	12.77	12.76	12.79	12.81
R_i [$\text{m}\Omega$]	3.60	3.60	3.63	3.68	3.55
Weight [kg]	18.41	18.22	18.36	18.14	18.14

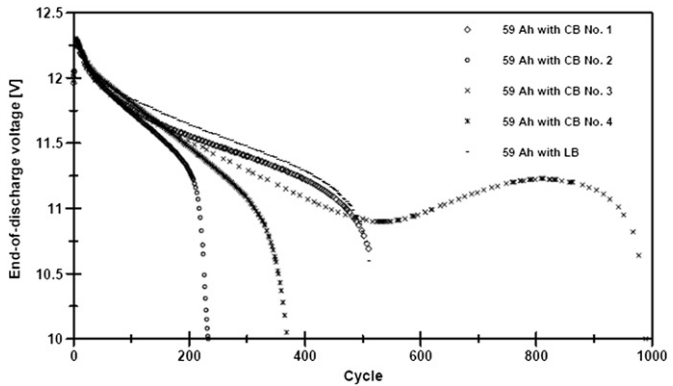


Fig. 4. Cycles with 17.5% depth of discharge: Comparison of 59 Ah enhanced flooded batteries with the different CBs and the LB in the NAM.

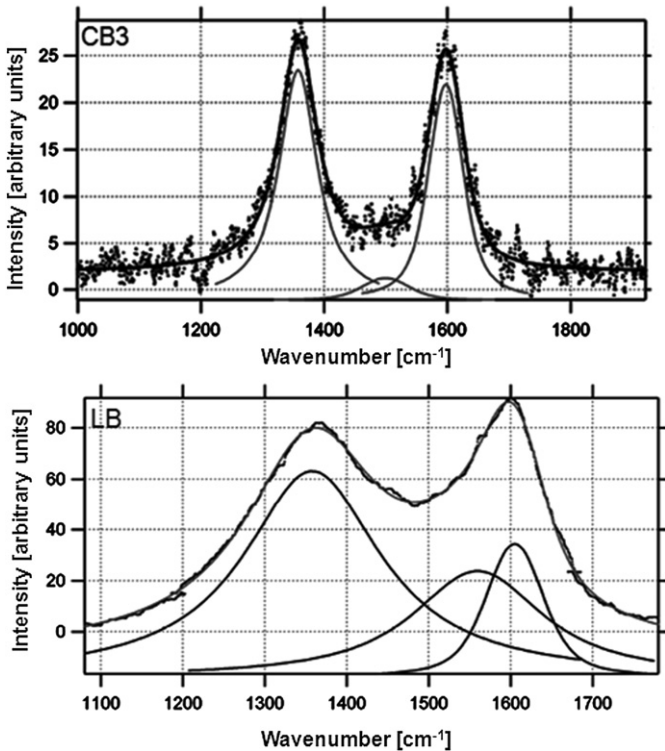


Fig. 3. Raman spectra of CB No. 3 and LB.

consumption levels of the batteries with CB No. 2 and 3 it becomes clear, that there is no correlation between impurity level and water consumption.

In a previous study of Lam et al. [22], the influence of trace elements in lead on oxygen- and hydrogen gassing rates of VRLA-batteries was investigated. Gassing not only leads to increased water loss, it can also homogenise a stratified electrolyte [23].

Lam et al. chose the Plackett–Burman design for determining maximum acceptable levels (MALs) of different elements [22]. The

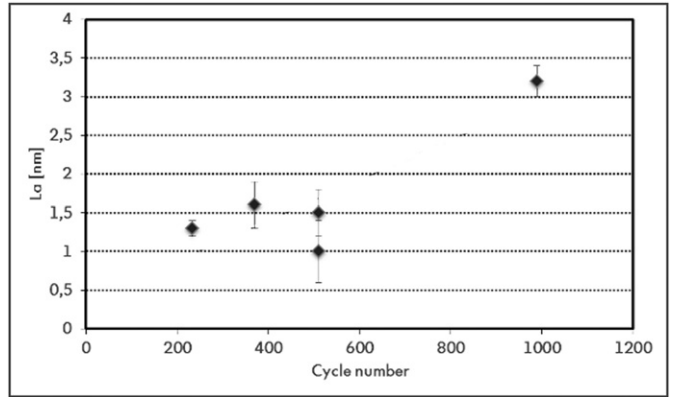
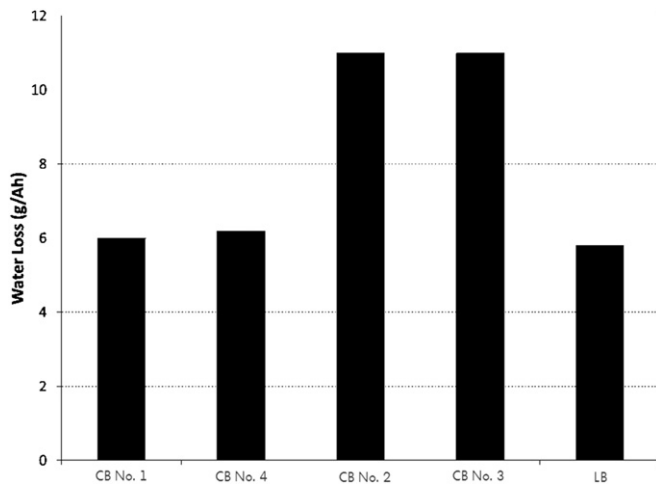


Fig. 5. Correlation between cycle number and L_a values.

Table 5
Impurities [ppm] of CBs and LB.

	CB No. 1	CB No. 2	CB No. 3	CB No. 4	LB
Impurity [ppm]					
Fe	7.5	10	7	31	2
Co	<0.1	<0.2	<0.2	<2	<0.3
Cu	<0.3	<0.2	<0.2	10	<0.3
Cr	<0.2	<0.3	0.5	<2	<0.3
Ni	<0.42	1	0.8	94	<0.3
Mn	<0.1	<0.2	<0.2	<2	0.3

**Fig. 6.** Water consumption values of the different CBs and the LB.

MAL of iron, nickel, and copper is 10 ppm. Based on this and the fact that the electrolyte of the batteries with CB No. 1, 2, 4 and the LB show similar acid stratification ($\Delta\rho = 0.075 \text{ kg L}^{-1}$, $\Delta\rho = 0.080 \text{ kg L}^{-1}$, $\Delta\rho = 0.062 \text{ kg L}^{-1}$, $\Delta\rho = 0.065 \text{ kg L}^{-1}$, see Table 6), Based on this and the fact, that the electrolyte of the batteries with CB No. 1, 2, 4 and the LB shows similar acid stratification (... see Table 6), we feel that the levels of impurities in CB No. 1, 2, 4 and the LB do not significantly promote gassing (mind that even the CB No. 4 with the highest impurity content does not lead to more gassing and therefore minor stratification!) and therefore it will not have an important impact on cycle life under our test conditions (PSOC conditions) – note also that 0.5 ppm impurity in the carbon will be 0.005 ppm in the NAM. On the other hand, CB No. 3 shows less acid stratification ($\Delta\rho = 0.021 \text{ kg L}^{-1}$). In this particular case, minor stratification is possibly due to a fast distribution of the current by the higher ordered carbon-network, which leads to a uniform release of acid on the plates of the battery. A more detailed investigation of synergistic effects in reducing acid stratification in flooded lead acid batteries is under way.

It is common belief that close attention must be paid to the purity of carbons that are included into the NAM [5]. However, the above results show that this view has to be revised: The amount of

carbon which is incorporated into the NAM is decisive for the cycle live. Only high levels of impurities promote gassing and lead therefore to increased water loss and might homogenize the electrolyte. Even the higher content of iron, copper and nickel in CB No. 4 does not cause more gassing in the electrolyte. These results show that impurities are not the only factor. It is rather important to consider structural carbon properties regarding the correlation between cycle life and material properties. The degree of order of the respective CBs seems to influence cycle life strongly. In addition to the degree of order and impurity content, also parameters like porosity, particle size, and dry powder resistivity (see Table 1) will have an impact on cycle life.

In addition to the high degree of order, CB No. 3 (Table 3) has, in contrast to the other CBs, the largest particles (Table 1). However, bigger particles tend to less agglomeration [24]. Therefore, the particles are probably more homogeneously distributed in the NAM. This leads to a stronger wetting of the lead surface, a shortening of diffusion paths, and presumably a more efficient use of the whole negative plate. Similar observations were made in a study about lithium ion batteries. In this study it was reported about high durability when the carbon particles are well dispersed in the electrodes [25]. Furthermore, CB No. 3 has a low dry powder resistivity and in contrast to the other carbons medium porosity (Table 1).

CB No. 2 shows nearly the same porosity, slightly smaller particles, and similar resistivity (cf. Table 1) similar to CB No. 3, but with a lower degree of order (Table 3) and breaks earlier down in cycling with 17.5% DoD (Fig. 4). CB No. 1 is more ordered as CB No. 2 (Table 3), shows more porosity (Table 1), and has the same resistivity. Therefore it reaches about 500 cycles in the 17.5% test.

The battery with the CB No. 4, which shows, similar to CB No. 1, increased ordering (Table 3) and higher porosity (Table 1), reaches in the test with 17.5% DoD only 375 cycles. This could be explained as follows: CB No. 4 contains a higher degree of impurities and the resistivity of this carbon is the highest (Table 1) by orders of magnitude, which is due to the surface modification which affects the ability of this carbon to participate effectively in the Pb^{2+} reduction to Pb during charging of the battery. Furthermore, the particles of CB No. 4 are smaller compared to other CB particle sizes (Table 1). These primary particles will tend to agglomerate more easily than the bigger ones [24]. Kuroda et al. found that it is difficult to make carbon aggregates disperse homogeneously into cathode materials of lithium ion batteries, since they easily flocculate due to their large surface area [25]. In this context, they reported about deterioration of battery performance. According to this, the bigger particle agglomerates result in worse dispersion of the CB No. 4 within the negative electrode. This results in a reduced cycle life.

The battery with the LB reaches, as the battery with CB No. 1, about 500 cycles in the test with 17.5% DoD (Fig. 4), though the LB shows less ordering (Table 3) and small pores (Table 1), where the LB shows a low dry powder resistivity (Table 1). The reason for longer cycle life is the low LB resistivity (Table 1), which seems to play a crucial role for the cycle life.

Further differences in microstructure in the carbon black are presently under investigation.

Table 6
Acid density values ρ [kg L^{-1}] before and after cycling on the top and the bottom of the plate.

	Battery (CB No.1)	Battery (CB No. 2)	Battery (CB No. 3)	Battery (CB No. 4)	Battery (LB)
ρ Before cycling [kg L^{-1}]	1.287 (± 0.002)	1.297 (± 0.018)	1.298 (± 0.014)	1.295 (± 0.021)	1.289 (± 0.003)
ρ After cycling (top) [kg L^{-1}]	1.125 (± 0.016)	1.129 (± 0.047)	1.195 (± 0.013)	1.129 (± 0.019)	1.131 (± 0.009)
ρ After cycling (bottom) [kg L^{-1}]	1.199 (± 0.019)	1.209 (± 0.018)	1.217 (± 0.024)	1.192 (± 0.012)	1.194 (± 0.042)

4. Conclusions

Depending on their modification, carbon blacks included in the NAM increase the cycle life of flooded lead-acid batteries by up to a factor of two. Different material properties, such as degree of order, porosity, particle size, dry powder resistivity, and impurities work together – the correct combination of these properties influence significantly the battery-cycle life. Specifically, a high degree of order of the included CB in the NAM influences to a great extent battery lifetime. Low levels of impurity (<100 ppm) will only have a minor effect on battery life. Besides parameters such as porosity, dry powder resistivity and average particle size, the degree of order of a carbon will influence the cycle life to a huge extent. However, the former material characteristics should not be ignored, because synergistic effects may be possible. Further studies should look more closely to the influence of carbons containing micro- or mesopores, different average particle sizes, as well as conductivities on battery cycle life.

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Glossary

AGM: Absorbant Glass Mat
 BET: Brunnauer Emmet Teller
 CB: carbon black
 DoD: depth of discharge
 EFB: enhanced flooded battery
 HRPSOC: high rate partial state of charge
 HRTEM: high-resolution transmission electron microscopy
 LB: lamp black
 NAM: negative active mass
 MAL: maximum acceptable levels
 PSoC: partial state of charge
 SAED: selected area electron diffraction
 SEM: scanning electron microscopy
 TEM: transmission electron microscopy
 VRLA: valve regulated lead acid battery
 L_c : medium lateral crystallite size [nm]
 OCV: open circuit voltage [V]
 R_i : internal resistance [mΩ]
 ρ : acid density [kg L⁻¹]